

Spin traps switch the energy transfer to electron transfer reaction in the new Ru complex

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A novel ruthenium complex, **Ru-2**, has been synthesized. It is composed of three bipyridyl ligands, one of which is modified and has two hydroxamate groups. Photoexcitation of the complex with blue light ($\lambda = 477$ nm) leads to the formation of a long-lived nitroxyl radical on hydroxamate as was detected and characterized by ESR. In anaerobic conditions, the radical was not formed, suggesting that a reactive oxygen species is required for generating the nitroxyl radical. The quenching of the excited state of ruthenium bipyridyl complexes by molecular oxygen can generate either singlet oxygen via **energy transfer** or superoxide radical via **electron transfer**. In this latter case the superoxide radical is confined in a cage complex (vide infra). Singlet oxygen, generated via energy transfer from Ru(II) in its excited state, is the reactive species that is responsible for the oxidation of the hydroxamate group to its corresponding nitroxyl radical. This was confirmed by using a specific spin trap TEMP, quencher (sodium azide) and by following the kinetics of the nitroxyl radical formation in deuterated solvents. Moreover, we can turn on the electron-transfer pathway by liberating superoxide radicals and producing a strong oxidant, Ru(III), from the collision "cage" complex proposed earlier (Zhang, X.; Rodgers, M. A. J. J. Phys. Chem., 1995) This was achieved using compounds with either chemical (PBN, DMPO) or enzymatic (superoxide dismutase) affinity to superoxide radicals. Thus, the rate and yield of the nitroxyl radical formation in the novel ruthenium complex can be increased by almost thirty times.

